

## Purification/Decolorization Treatment for Fatty Nitriles

### Field of the Invention

The present invention generally relates to a new purification and/or decolorization treatment process for fatty nitriles.

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### Background of the Invention

Fatty nitriles, those derived from fatty acids, are important articles of commerce which are useful in the preparation of insecticides, gelling agents, fabric softeners and wetting agents. They may be hydrogenated to form primary, secondary or  
10 tertiary amines, particularly the valuable aliphatic amines.

A common commercial method for obtaining nitriles is the catalytic dehydration of fatty acids in the presence of ammonia. This method, however, yields, in addition to the nitriles, many troublesome by-products, including different amines that  
15 contribute color and odor, and also amides. Such impurities, particularly the amides, must be reduced to a low level before the nitriles may be used in the various processes that produce the valuable products. Amides are known to be poisons for hydrogenation catalysts.

20 There are many teachings in the prior art that deal with the purification of nitriles, usually by removing those by-products of the nitrile synthesis reaction, primarily color bodies and amines, which are close in boiling point to the nitrile product and, therefore, difficult to remove by distillation. In the process of U.S. Patent No. 2,622,097 to Osborne, impure acrylonitrile is first passed through activated carbon  
25 then through a moistened ion exchange material which may be regenerated by the use of acid, but which is substantially free of acid when used.

CONFIRMATION COPY

The process of U.S. Patent No. 2,943,049 removes hydrocarbon compounds of nitrogen, particularly amines, from hydrocarbon mixtures using various siliceous minerals, including bentonite which have been completely hydrogen ion exchanged.

- 5 U.S. Patent No. 3,206,497 to Oblad discloses the separation of a nitrile from a mixture containing other nitrogen-containing compounds of basic character by contacting the mixture with a metal halide which precipitates out the basic nitrogen compound.

10 In the process of U.S. Patent No. 3,262,966 to Higgins, Jr. et al, activated alumina is used to remove carbonyl compound impurities from acrylonitrile.

In the process of U.S. Patent No. 4,147,717 to Kershaw, amines are removed from adiponitrile by using a variety of materials, including bentonite in the presence of acid, with the adiponitrile preferably containing from 1 to 10% by weight of water.

15 The process of Great Britain Patent No. 1,223,790 to Kuhlmann effects removal of impurities from nitriles, particularly heterocyclic compounds containing one or more nitrogen atoms in the ring, by using various adsorbents, including montmorillonite.

German Pat. No. 1,046,601 to Cadus et al discloses a process for the purification of adiponitrile using a solid adsorbent such as silica gel, activated carbon or clay.

20 It is also known to the art that organic cations, particularly amines, may replace cations which were originally present on clay surfaces and that there is a strong preference of the clay for the organic cation. Clay Colloid Chemistry, Van Olphen, H., Wiley, 2nd Ed., 1977 is one reference that provides such a teaching.

The present invention addresses a problem not specifically addressed by any of the above references comprising the presence of amides as an impurity in the nitriles. Nitriles produced via the above reaction in which fatty acids are dehydrated in the presence of catalyst and ammonia may contain amides in solution up to the saturation point (about 0.9 wt. % amide). The prior art method for removing these amides has been simple distillation, which is sometimes feasible because of the significant difference in boiling points between the nitriles and amides. If one, however, has to work with nitriles of mixed chain lengths, distillative separations may not always be possible due to the fact that amides of shorter chain length co-distill with the higher chain length nitriles. Distillation, also, requires considerable energy input which in an era of increasing energy costs becomes increasingly unattractive.

The present inventors have discovered a process that effects removal of amides from solution with nitriles without employing distillation.

#### 15    Summary of the Invention

The primary objective to which the present invention is directed is the removal of amides from a solution of nitriles and amides. In one embodiment, the invention contemplates a process for the removal of impurities comprising amides, but which may include other impurities such as amines, from a solution of the nitriles and impurities. A reaction mixture is first formed and to that reaction mixture, 0.5 to 3wt% of diluted H<sub>2</sub>SO<sub>4</sub> (approximately 60%) is stirred in at room temperature and atmospheric pressure for a time effective for the removal of the amide impurities. Typically, after about 30 minutes, the amide impurity is removed into the lower, dark acid layer, probably as a salt. The remaining nitrile, after decantation or filtration, is still colored but is nearly free of amide. In a second step, at room temperature or at a temperature of up to ~80°C, color can be removed from the

nitrile by stirring the acid-washed nitrile with 0.5-5 wt% of an adsorbent such as clay (bentonite), charcoal, zeolitic type materials, mixtures thereof and the like.

### Detailed Description of the Invention

Nitrile feedstocks of primary interest to the present invention fall into one of the three types comprising "coco-nitrile", "tallow-nitrile" and "oleo-nitrile". The compositions of these types, in terms of percent of fatty nitriles of various chain lengths, are in accordance with the following:

No. of Carbons	6	8	10	12	14	16	18	14'	16'	18'	18''
Coco-nitrile	.5	8	7	50	18	8	1.5			6	1
Tallow-nitrile				1	3	29	23	1	3	37	1.5
Oleo-nitrile				.5	3.5	4	5	1.5	5	76	3

The superscripts ' and '' denote, one unsaturated and two unsaturated bonds respectively, per molecule.

The amide impurity with which the present invention is particularly concerned has the chemical structure:



where R may comprise a wide variety of hydrocarbon or hydrocarbon-based groups, particularly

long chain aliphatics. The term "long chain" denominating compounds with, on average, 6 or more, preferably 8 or more, and most preferably 10 or more carbon atoms. The reaction mixture of the invention will include such amides. The amide content in the nitrile may be as high as its solubility limit (up to about 0.9 wt. % at room temperature) or even greater, whereupon at least a portion of the amides would appear as particulate matter. The average molecular weight of the amides in the above feedstock is assumed hereinafter to be 270. Amides of that molecular weight are referred to as "tallow amides". There may also be a wide variety of other impurities, primarily amines, which may impart color and odor to the nitriles.

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The present invention is directed is the removal of amides from a solution of nitriles and amides. In one embodiment, the invention contemplates a process for the removal of impurities comprising amides, but which may include other impurities such as amines, from a solution of the nitriles and impurities. A reaction mixture is first formed and to that reaction mixture, 0.1 to 15 wt% of a strong acid (for e.g., a 60%  $\text{H}_2\text{SO}_4$ ) is stirred in at room temperature and atmospheric pressure for a time effective for the removal of the amide impurities. Typically, after about 30 minutes, the amide impurity is removed into the lower, dark acid layer, probably as a salt. The remaining nitrile, after decantation and/or filtration, may still be colored but is nearly free of amide. In a second optional color-removing step, at room temperature or at a temperature of up to  $\sim 80^\circ\text{C}$ , color can be removed from the nitrile by stirring the acid-washed nitrile with 0.5-5 wt% of appropriate adsorbent such as clay (bentonite), charcoal and or zeolitic type materials.

Although not limiting the invention to a particular hypothesis, it is believed that the addition of acid to the nitrile containing amide impurities causes the precipitation and/or separation of the amide impurities as acid salts which can be easily removed from the reaction mixture.

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The choice of acid to achieve the above is very critical. First, the acid must be strong enough to drive the formation of the amide salts. Water content of the reaction mixture must be controlled so that there is enough to promote insolubility of the acid and its amide salt in the nitrile. Too little water, in the case of a  
5 dehydrating acid such as sulfuric, can also lead to "burning" or the promotion of dark colors, especially at elevated temperatures. Hence it is important in the process of the present invention to employ larger amounts of a diluted strong acid rather than smaller amounts of a stronger/concentrated acid. To effect maximum amide removal there should also be an amount of acid in excess of the  
10 stoichiometric amount required in order to provide a vehicle for the amide salt and because a portion of the acid is consumed in the course of the various reactions.

Examples of strong acids employable in the context of the present invention include but are not limited to sulfuric acid, hydrochloric acid, hydrobromic acid,  
15 perchloric acid, nitric acid, fluorosulfonic acid, methanesulfonic acid, trifluoromethanesulfonic acid, toluenesulfonic acid, phosphoric acid and mixtures thereof. Typically, the acid is diluted in an amount such that its combination with an amount of water that allows an amide salt to remain substantially insoluble in excess aqueous acid. Preferably, 0.1 to 15 wt% of acid is employed. In another  
20 embodiment, up to 5 wt% of acid is employed. In still yet another embodiment, 0.5 to 2 wt% acid is employed.

The conditions at which the process of the present invention is carried out are not critical. The present inventors have noticed, however, that the color of the acid-  
25 washed nitrile deepens as the sulfuric acid concentration increases or if the temperature is raised. Optimum conditions appear to be obtained with 60-70%  $\text{H}_2\text{SO}_4$  at about 25°C. A temperature of from about 15° C to about 100°C and reaction time from about 5 minutes to about 4 hours are the contemplated normal

operating conditions for a fatty nitriles feedstock having carbon chains of from about 10 to about 22 in length.

After the nitrile is made, 0.5 to 3 wt% of dilute  $\text{H}_2\text{SO}_4$  (approximately 50-70%), with  
5 or without 0.5 to 5% of an optional filter aid, is stirred in at room temperature and atmospheric pressure for a time effective for the removal of the amide impurities. The optional filter aid may be such things as clay, silica or diatomaceous earth. Typically, after about 30 minutes, the amide impurity is removed into the lower, dark acid layer, or is adsorbed onto the filter aid, probably as a salt. The remaining  
10 nitrile, after decantation and/or filtration, may still be colored but is substantially free of amide.

In a second optional color-removing step, at room temperature or at a temperature of up to 30 to about 100°C, color can be removed from the nitrile by stirring the acid-washed nitrile with 0.5-5 wt% of a color adsorbent such as clay (bentonite),  
15 charcoal and/or zeolitic type materials. This second step can be carried out by means of a slurry of the mineral and the acid-treated nitrile solution or by passing the nitrile over an adsorbent bed. Bentonite clay is an excellent choice for the slurry method and readily disperses in a liquid medium. The slurry may be maintained for the course of the reaction by agitating means such as a stirrer or mixer.

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A key step in the process of the present invention is the separation of the nitriles having a reduced content of impurities and improved color from the reaction mixture. This can be accomplished by draining the thick, liquid amide salt layer from the upper purified nitrile layer or by decantation of the nitrile layer.  
25 Alternatively, one may add an adsorbent along with the acid treatment and filter out the adsorbent/amide salt/excess acid by means of one or more filter assemblies. Such an assembly is basically a filter medium, such as a filter cloth, where the feedside is exposed to the fluid to be filtered, and the filtrate side is exposed to a

lower pressure. Thus, either pressure or vacuum filtration may be employed with any suitable filtering medium.

The following nonlimiting example is presented to illustrate the present invention.

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#### EXAMPLE

To a 500 g portion of Arneel® TM (untreated tallow nitrile) at ambient temperature under nitrogen was added 5.0 g (1.0 wt%) of 60% sulfuric acid with rapid stirring.  
10 After 30 minutes, the dark mixture was allowed to stand for another 30 minutes before the upper nitrile phase was decanted from the dark oily lower layer. The acid-treated nitrile was then stirred with 2.0 wt% of bentonite clay at 80° for 30 minutes before filtration. The changes in color and amide content are shown below.

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Arneel TM after Acid Treatment and Decolorizing

Analysis	Before treatment	After treatment
Gardner color	6.8	<1
Amides, wt% by IR	0.19	<0.02 (undetectable)